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Inhibition of Combustion and Explosion of Methane–Air Mixtures in the Presence of Coal Dust

V. V. Azatyan[a, *], V. M. Prokopenko[b, **], and S. K. Abramov[b]

[a] *Institute for System Research, Russian Academy of Sciences, Moscow, Russia*
[b] *Merzhanov Institute of Structural Macrokinetics and Materials Sciences, Russian Academy of Sciences, Moscow oblast, Chernogolovka, 142432 Russia*
**e-mail: vylenazatyan@yandex.ru*
***e-mail: vprok48@mail.ru*

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Abstract—Coal dust was shown to promote the combustion of methane–air mixtures, reducing the lower concentration limit of flame propagation and making combustion progressive (coal of different grades was used). An inhibitor has been proposed and tested to prevent the ignition of methane initiated by a spark, suppress flame propagation, and prevent its transition to an explosion. The results also show that coal dust-stimulated methane combustion, as well as in the absence of dust, is a branched-chain process that can be completely suppressed by inhibition.

Keywords: ignition, combustion, explosion, detonation, gases, methane, chain reactions, reaction rate, coal dust, inhibitors, mines, explosion safety

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The importance of developing efficient methods for preventing the ignition and explosion of methane–air mixtures is primarily dictated by the safety of work in coal industry. To prevent the ignition and explosion of methane in mines, various engineering facilities are used: ventilation, flame and spark arresters, etc. For a long time, it was generally accepted that combustion at atmospheric pressure under conditions of self-heating is determined only by the heat released during the combustion. The role of reaction chains was ignored and even denied (e.g., [1–3]). For example, in monograph [2], where unlike [1], the role of chains is not denied, flame propagation and detonation considered without taking into account the chain mechanism of the reaction. At present, however, it is known that the activation energies of the reactions of molecular compounds among themselves are very large, for example, for the reactions of H_2 and CH_4 with O_2, they exceed 220 kJ/mol. Therefore, the rates of these intermolecular reactions are extremely low; the reactions are practically not even accompanied by self-heating. Hence it was obvious that the combustion of methane, as well as of other flammable gases, occurs only by the chain mechanism, with participation of free atoms and radicals at any pressures and temperature conditions. This conclusion was confirmed by experiments (e.g., [4–6]).

The chain nature of combustion opens up an opportunity to control the process by changing the competition of the main stages, including acceleration of reaction chain termination using small additions of inhibitors. Combustion inhibition with the help of additives had long been known before the discovery of chain processes [7]. However, the effect of additives was considered to be merely the result of strong dilution and increased heat capacity.

Chemical inhibition agents differ from the above-mentioned technical methods in being more efficient due to the fact that the rate of combustion depends exponentially on the difference in the rates of the competing branching and chain termination reactions [8]. Therefore, by reducing the difference between these rates by increasing the termination rate, the inhibitor greatly exponentially slows down the combustion process.

It is also known that coal dust that is present under mining conditions promotes methane combustion [9, 10]. Experiments and tests performed in small (3.5 L) and large (4, 29 m^3) volumes [11, 12] showed that the explosion of methane–air mixtures also occurs in the absence of coal dust.

The purpose of this work was to propose an inhibitor that prevents the ignition and explosion of methane–air mixtures, to examine the tendencies in suppression of ignition, combustion, and explosion, and to study the role of coal dust in methane combustion

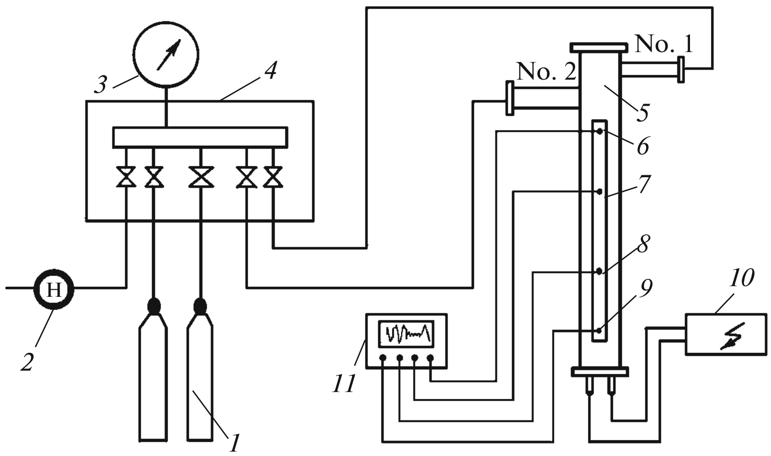

Fig. 1. Stand with a vertical reaction tube: (*1*) gas cylinders, (*2*) gas inlet valve, (*3*) pressure gage, (*4*) manifold valves, (*5*) reactor, (*6–9*) photosensors, (*10*) ignition unit, and (*11*) oscilloscope.

and explosion. Under the action of small chemically active inhibitor additives, ignition is prevented and flame propagation efficiently suppressed due to the fact that small additions of these compounds vigorously react with active species (free atoms and radicals), forming the products that cannot participate in chain combustion. Thus, the reaction chains are broken and combustion is blocked. As an inhibitor we used trifluoromethane. This compound is environmentally friendly and recommended by regulatory documents as a fire extinguishing agent [11]. Here we also used a tendency revealed in our previous study [12]: nonadditive enhancement of the combined effect of the inhibitor and inert gas (nitrogen).

EXPERIMENTAL

A stand with a vertical reaction tube with a length of 2 m and a diameter of 10.1 cm is schematically shown in Fig. 1. Combustible mixtures were prepared in a mixer cylinder at partial pressures 24 h before the experiments. The reaction mixture was fed in the reactor evacuated to a pressure of 1 bar. Ignition was initiated by a spark with an energy of 3.6 J using electrodes lying at the lower end of the reactor. The flame moving through the reaction tube was recorded using four photosensors located along the reactor at certain distances from the lower end of the tube and connected to a Tektronix TDS–3014 four-channel oscilloscope.

For experiments with coal powder, a portion of the powder was preliminarily placed in the upper part of the reactor. After air evacuation from the reactor, the mixture was slowly supplied through pipe *1* until the pressure in the reactor reached 0.9 bar. Then the gas was quickly fed through nozzle *2* from the mixer (with nozzle *1* closed) to a pressure of 1 bar, and the coal powder (15 g) lying on the site of nozzle *2* was thrown by the gas flow into the reactor. Ignition was initiated after 3–5 s required for the powder to spread throughout the reactor volume.

The time dependences of the flame path were plotted based on the known distances from the photosensors to the ignition site and the time of flame propagation past each of them (x–t diagrams of flame propagation). Several experiments were performed for each mixture composition to check the reproducibility of results.

RESULTS AND DISCUSSION

The majority of experiments were performed with both ends of the reaction tube closed. This ensured homogeneity of the mixture composition throughout the pipe and, at the same time, made it possible to monitor the inhibition effect. The closed ends certainly inhibited the propagation of the combustion wave, but in this case, the object of study was the inhibition process itself, and the state of the ends (open or closed) was unimportant.

Figure 2 shows, as an example, the oscillograms of the flame front running past the sensors during the combustion of 6% methane in air in the absence of coal dust and inhibitors. After the mixture was ignited in the lower part of the reactor, the flame was recorded in the area of the first sensor. Figure 2 shows that by the time the combustion zone reached the second sensor, there was no flame in the zone of the first sensor as combustion had already been completed at the first sensor. After the second sensor, flame is recorded by the third and then the fourth sensor. Note that sequential recording of flame movement along the reactor demonstrates the layer-by-layer nature of flame propagation in good agreement with combustion theory [1–3]. When the methane content in the initial mix-

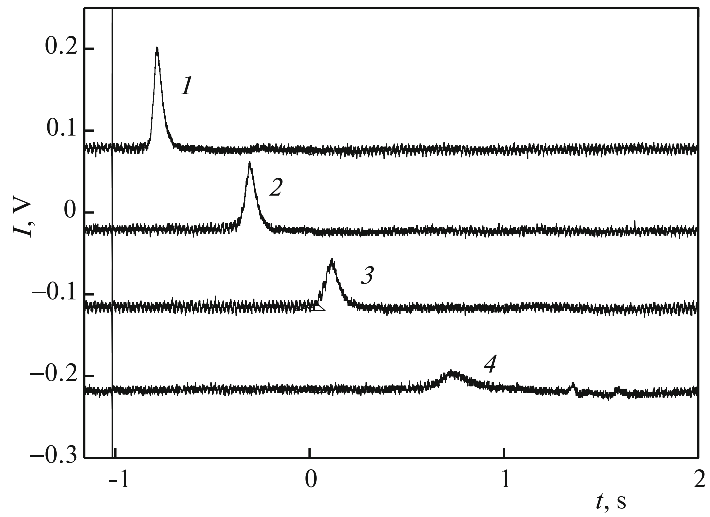

Fig. 2. Oscillograms of combustion of a 6% methane–air mixture near sensors *1*, *2*, *3*, and *4*.

ture increases, the flame rate increases, passing through a maximum in the region of 8% methane in air. When the outlet end of the reactor is open (Fig. 3), the flame rate is higher, and acceleration progresses.

Effects of coal dust and inhibitor. The following grades of coal dust were used: KZh (fat coking coal), anthracite, and graphite. Figure 4 shows a histogram of anthracite powder recorded on a VA Instalt laser particle analyzer. The particle size varied mainly from 6 to 20 μm.

Figure 5 presents examples of *x*–*t* diagrams from experiments with 5.5% methane in the absence and presence of coal dust. It can be seen that near the lower concentration limit in the presence of coal dust, combustion proceeds slightly more actively than in the absence of dust; i.e., coal dust promotes combustion. The promoting effect of coal is also observed during combustion of compositions between the concentration limits. However, in the vicinity of the upper concentration limit, the effect of the powder is not observed.

Coal dust promotes combustion over the entire concentration area of combustion. A comparison of curves *1*, *2* with curves *3*, *4* in Fig. 6 shows that flame propagation becomes progressively faster when coal dust is added; i.e., coal dust promotes combustion. The results of studies of the effect of coal dust and inhibitory additives on combustion are presented in Table 1 and Figs. 5–7. According to Fig. 7, as the mixture is enriched with methane, the influence of coal dust decreases near the upper limit.

Thus, it was concluded that methane–air mixtures (except those with high and low fuel contents) pass from combustion to explosion even in the absence of coal dust. Coal dust promotes the combustion and stimulates the transition to explosion. The proposed inhibitor prevents this transition, suppresses flame propagation, and prevents ignition; it also hinders spark ignition, increasing the required ignition energy. The combined composition with nitrogen is more efficient.

The addition of an inhibitor suppresses combustion (Table 1). A comparison of the graphs without inhibitor in Figs. 3 and 6 (*3*, *4*) with the graphs in Fig. 8 with a 6% inhibitor additive in an 8% mixture of CH_4 with both 6 and 10% nitrogen shows that the slopes of the curves on the *x*–*t* diagrams decrease; i.e., the flame rate decreases. In addition, in the presence of an inhibitor, the concentration range of ignition and flame propagation narrows: the lower concentration limit increases. Addition of nitrogen to this 8% mixture of CH_4 with 6% inhibitor to 15% leads to complete

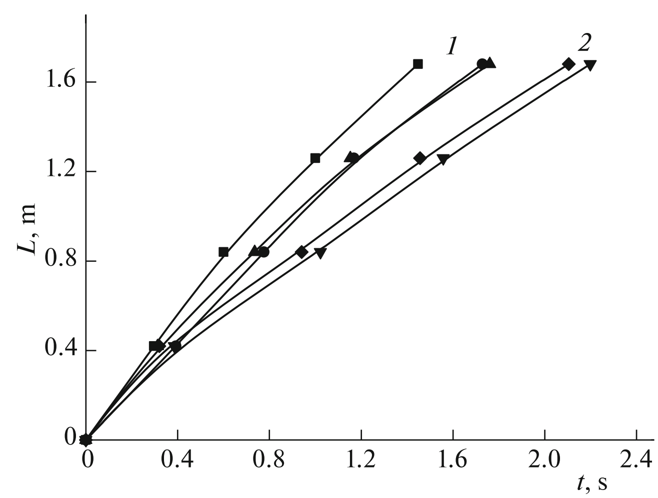

Fig. 3. *x*–*t* Diagram of combustion of a methane–air mixture with 10% CH_4 in air with (*1*) open and (*2*) closed ends.

Laser particle analyzer
VA Instalt

MicroSizer 201

Saint Petersburg
Russia

Operator:		Comment:			
File name:	Azatyan Prokopenko coal.fms				
Data:	May 28, 2013	Calculation by:	Fraunhofer	Range:	(0.60–150) μm
Time:	10:48:25	Ultrasound:	Power 200 W Time 0 s	Transmission coeff.:	100%

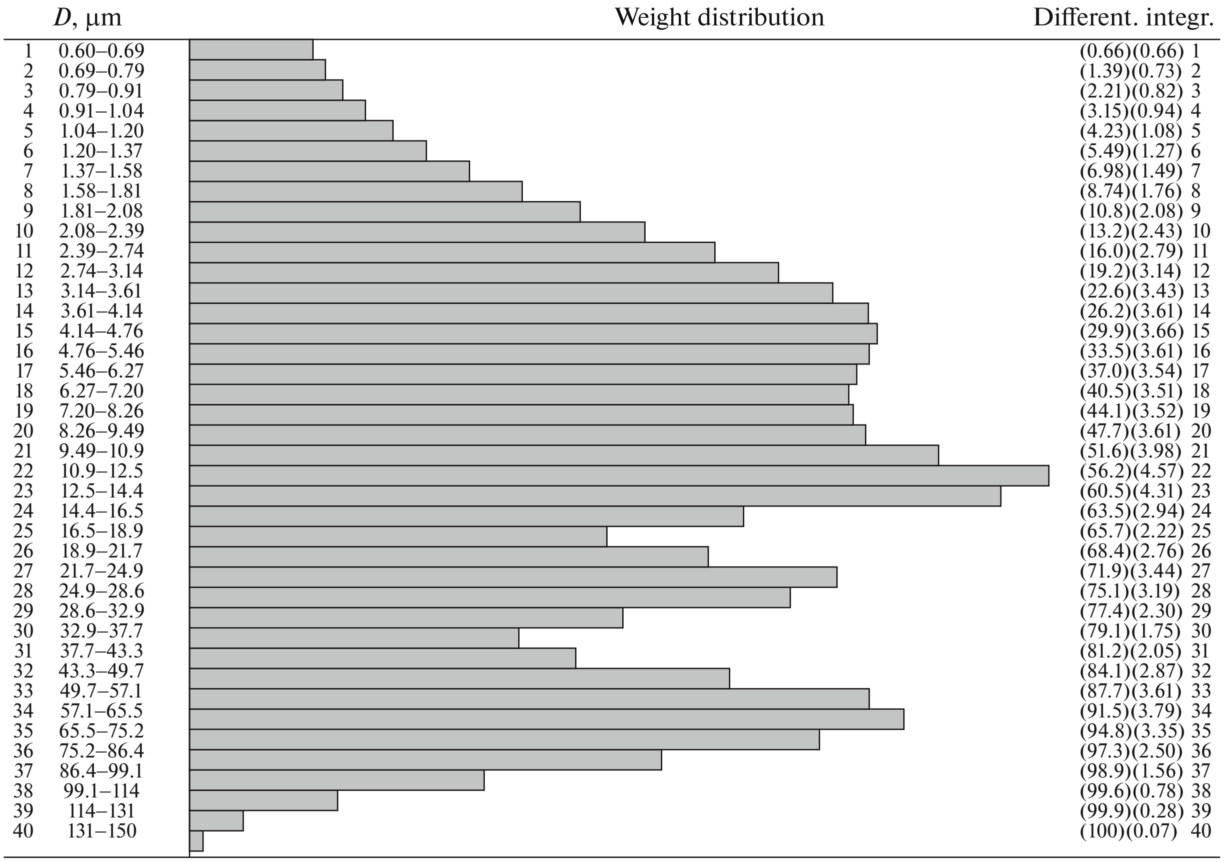

Table of correspondence between particle sizes (*D*, μm) and specified weight fractions

D, μm	1.97	3.26	4.78	7.06	10.3	14.1	23.2	40.1	62.3	150
P, %	10.0	20.0	30.0	40.0	50.0	60.0	70.0	80.0	90.0	100

Table of particle weight fractions (*P*, %) corresponding to specified particle sizes

P, %	0.00	0.00	2.80	10.2	18.1	31.2	49.1	61.6	76.0	84.2
D, μm	0.30	0.60	1.00	2.00	3.00	5.00	10.0	15.0	30.0	50.0

Fig. 4. Particle size distribution.

suppression of combustion. The results of the inhibitor effects are presented in Table 1.

The inhibitory effect of trifluoromethane is due to the reaction

$$H + CF_3H = H_2 + CF_3,$$

in which the chain carrier (atomic hydrogen) is replaced by the low-active CF_3 radical, which is not involved in the reaction chains of methane combustion.

Effect of powder. The results show that in the presence of coal dust, the lower limit decreases; i.e., the powder initiates the ignition of the mixture. The fact that coal particles do not burn themselves even in the presence of methane is obvious from the fact that outside the methane ignition zone with the initiating

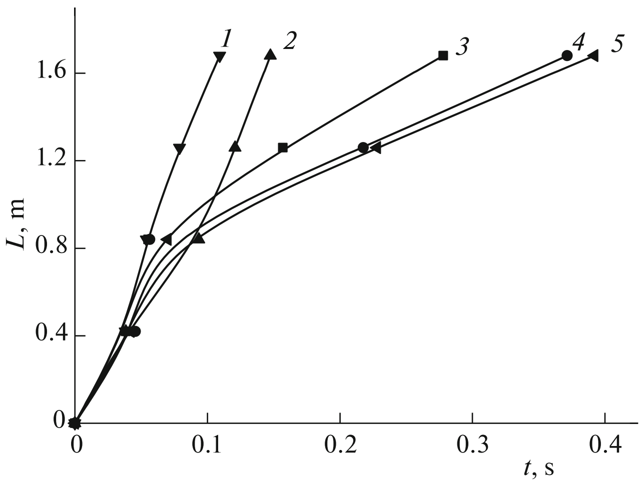

Fig. 5. *x–t* Diagram of combustion of a methane–air mixture with 5.5% CH_4 + 94.5% air; (*1*, *2*) 5.5% CH_4 + 94.5% air + coal; (*3–5*) without coal.

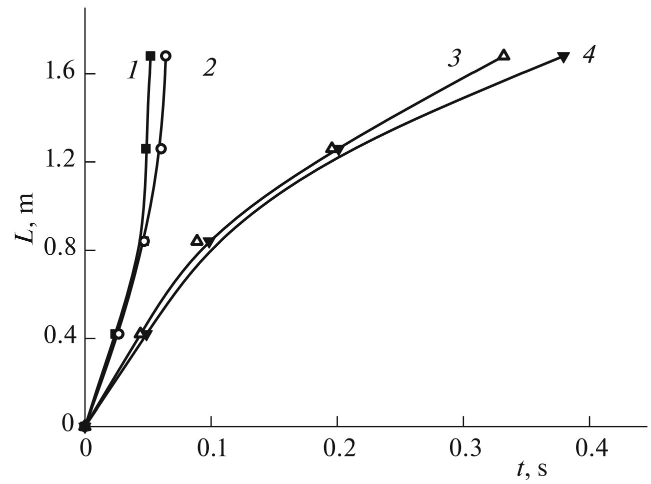

Fig. 6. Effect of coal powder on the flame rate and the character of its acceleration; *x–t* diagrams of flame propagation in mixtures with 9% methane in air (*1*, *2*) in the presence of coal dust and (*3*, *4*) in the absence of coal powder.

spark the dust remains unchanged. The mechanism of ignition initiation is that the hydrogen atoms formed from methane during the discharge are partially adsorbed on the surface. The reaction of O_2 with the adsorbed hydrogen atoms was also described, as a result of which the H atoms and the HO_2 and OH radicals appear in the gas phase. These species initiate the ignition.

A similar phenomenon was found in a mixture of hydrogen and oxygen in a quartz reactor [13, 14].

Inhibition at high pressures. The inhibitor effect on the combustion of a methane–air mixture (6% methane), igniting in the absence of an inhibitor, was tested on a stand with a reactor (Fig. 9) with a length of 15 m and a diameter of 10.1 cm. However, a mixture of 6% CH_4 + 8% Inh + 15% N_2 + 71% air could not be ignited in the pressure range of 0–6 atm when combustion was initiated by a spark discharge of 3.6 J. It was found that the mixture did not ignite over the entire pressure range and, therefore, the inhibitor efficiently prevents the combustion of methane also at elevated pressures.

To summarize, the results of this study show that combustion and explosion of methane–air mixtures take place only when a chain avalanche occurs regardless of the presence or absence of coal dust. Therefore, in the presence of an inhibitor, ignition and explosion do not occur. Thus, it was shown that methane combustion stimulated by coal dust is a branched chain

Table 1. Results of the experiments

Mixture	Without coal	Number of experiments	With coal	Number of experiments
3% CH_4 + 97% air	No combustion	2	No combustion	–
4% CH_4 + 96% air	No combustion	6	No combustion	–
5% CH_4 + 95% air	No combustion	6	Combustion	4
5.5% CH_4 + 94.5% air	Combustion	6	Burns better	3
(6–12)% CH_4 + 96% air	Combustion	21	Burns better	21
14% CH_4 + 86% air	No combustion	6	No combustion	6
15% CH_4 + 85% air	No combustion	6	No combustion	6
8% CH_4 + 5% Inh + 18% N_2 + 69% air	No combustion	7	No combustion	7
8% CH_4 + 6% Inh + 15% N_2 + 71% air	No combustion	7	No combustion	7
9% CH_4 + 6% Inh + 15% N_2 + 70% air	No combustion	3	No combustion	4

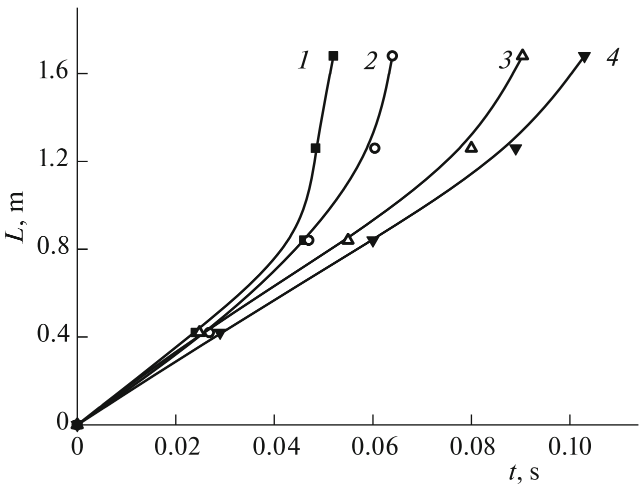

Fig. 7. *x–t* Diagrams of flame propagation in methane–air mixtures with coal dust: (*1*, *2*) 9% methane; (*3*, *4*) 11% methane.

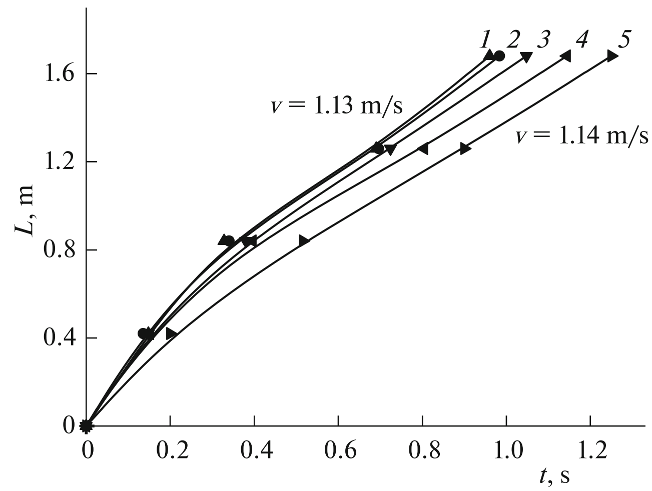

Fig. 8. *x–t* Diagrams of flame propagation in methane–air mixtures with 8% methane, with additions of (*1*, *2*) 6% and (*3–5*) 10% nitrogen and 6% inhibitor.

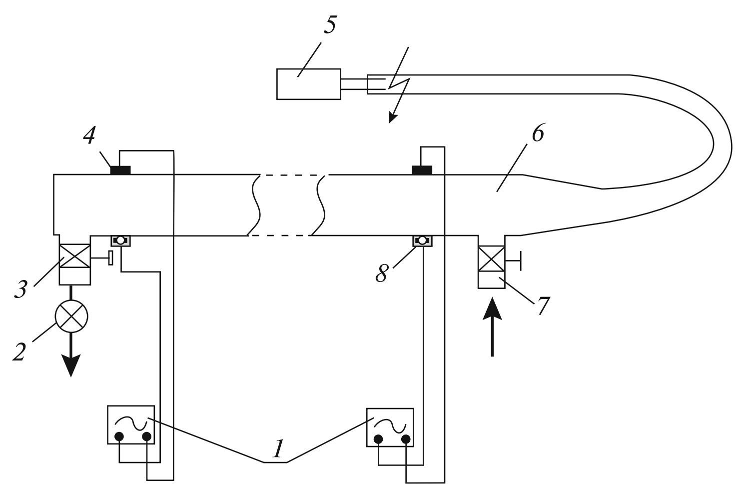

Fig. 9. Stand with a shock tube: (*1*) oscilloscopes, (*2*) pump, (*3*) valve, (*4*) photosensors, (*5*) reactor, (*6*) source of spark initiation, (*7*) outlet valve, (*8*) pressure gage.

process. Coal dust promotes combustion, which is manifested in the expansion of the ignition concentration region and conditions for the transition of combustion to explosion.

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CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. B. Lewis and G. Elbe, *Combustion, Flames and Explosions of Gases* (Mir, Moscow, 1968) [in Russian].
2. B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases* (Academic, New York, 1987).
3. D. A. Frank-Kamenetskii, *Diffusion and Heat Exchange in Chemical Kinetics* (Intellekt, Dolgoprudnyi, 2008; Springer, Heidelberg, 1995).
4. V. V. Azatyan, Russ. Chem. Rev. **62**, 1021 (1999).
5. V. V. Azatyan, Russ. J. Phys. Chem. A **85**, 1293 (2011).
6. V. V. Azatyan and G. R. Saikova, Russ. J. Phys. Chem. A **87**, 1615 (2013).
7. H. Devy, Phylos. Trans., 45 (1817).

8. V. V. Azatyan, Kinet. Katal. **17**, 533 (1976).
9. P. G. Demidov, Combustion and Properties of Combustible Substances (Vyssh. Inzhen. Pozhar.-Tekh. Shkola MVD SSSR, Moscow, 1975) [in Russian].
10. A. Ya. Korol'chenko, *Fire and Explosion Safety of Industrial Dust* (Khimiya, Moscow, 1986) [in Russian].
11. *Set of Rules: Fire Protection Systems, Fire Alarm and Automatic Fire Extinguishing Installations, Design Standards and Rules* (MChS Rossii, Moscow, 2009) [in Russian].
12. V. V. Azatyan, G. A. Balayan, V. M. Prokopenko, N. V. Chapysheva, and S. K. Abramov, Kinet. Catal. **57**, 573 (2016).
13. F. Haber and C. Alea, Z. Phys. Chem. B, No. 10, 193 (1930).
14. N. N. Semenov, in *Selected Works* (Ross. Akad. Nauk, Moscow, 2005), Vol. 3 [in Russian].